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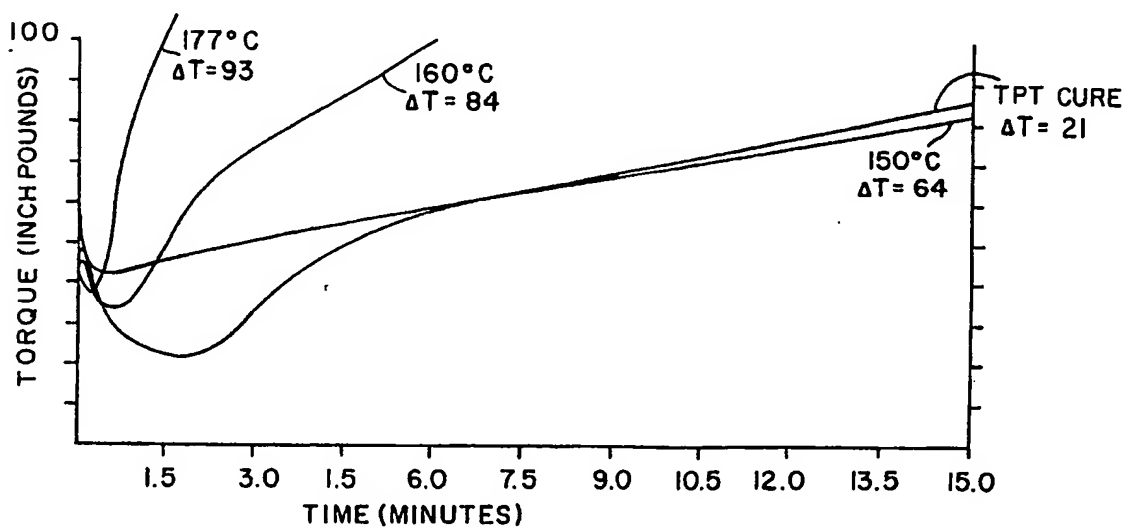
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⑥⑤ Cured perfluoroelastomers and their preparation.

⑥⑦ Perfluoroelastomers of tetrafluoroethylene, perfluoro (alkylvinylether) and a cure site monomer crosslinked with organic peroxide curing agent, and a process for their preparation.



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## CURED PERFLUOROELASTOMERS AND THEIR PREPARATION

Background of the Invention

Perfluoroelastomers have long been used in a variety of applications that require excellent resistance to high temperatures and chemical attack. A particularly outstanding class of fluoropolymers that has been used in elastomeric applications is that prepared from tetrafluoroethylene (TFE) and perfluoro (alkylvinylether) such as perfluoro (methylvinylether) (PMVE). To permit the crosslinking in these polymers that is essential to good elastomeric properties, a small percentage of termonomer is incorporated. A wide variety of such crosslinking sites has been used in the past, including those described in Brizzolara et al., U.S. Patent 3,682,872.

One particularly desirable terpolymer is that prepared from TFE, PMVE and a nitrile cure site monomer, such as perfluoro (8-cyano-5-methyl-3,6-dioxo-1-octene), or 8CNVE. This fluoropolymer has been cured in the past by organometallic compounds such as tetraphenyltin, which results in trimerization of the cyano function of the 8CNVE to triazine crosslinks. However, the high viscosity of the resulting compound and the slow rate of cure make the processing of this cross-linked material difficult. In addition, because the triazine crosslinks are prone to nucleophilic attack, they have inadequate resistance to aliphatic amines and water at elevated temperatures, particularly above 150 °C. Further improvement in these properties in the cured perfluoroelastomer has therefore been desired, along with improved processability. It would be also be desirable to eliminate the need for the toxic organometallic compounds often used in the curing operation.

Accordingly, continuing effort has been directed to the development of curing systems which result in improved physical properties in the cured elastomer and which permit curing at the least stringent conditions.

Summary of the Invention

The present invention provides a cured perfluoroelastomer which exhibits excellent hydrolytic stability, and a process for its preparation which eliminates the need for the organometallic curing compounds which have been used in the past.

Specifically, the present invention provides, in a cured perfluoroelastomer composition prepared from polymerized units of tetrafluoroethylene, perfluoro (alkylvinylether) and a nitrile cure site monomer, the improvement wherein the perfluoroelastomer is crosslinked with a carbon-carbon linkage.

The instant invention further provides, in the process for crosslinking a perfluoroelastomer of the type comprising polymerized units of tetrafluoroethylene, perfluoro (alkylvinylether) and a nitrile cure site monomer by contacting the perfluoroelastomer with crosslinking agent under reaction conditions, the improvement wherein the crosslinking agent comprises an organic peroxide and a peroxide coagent free radical source.

Brief Description of the Figure

The Figure is a graphical representation of the performance characteristics of cured perfluoroelastomers of the present invention as compared to those prepared using a previous curing system.

Detailed Description of the Invention

The present invention relates to terpolymers of tetrafluoroethylene, perfluoro(methyl vinyl ether) and a termonomer which provides a nitrile cure site in the terpolymer. While a wide variety of such termonomers can be used, a particularly preferred species is perfluoro (8-cyano-5-methyl-3,6-dioxo-1-octene). These terpolymers and their preparation are described in detail in Breazeale, U.S. Patent 4,218,092, hereby incorporated by reference.

The present invention is based on the discovery that the above perfluorinated terpolymers can be effectively crosslinked through the use of organic peroxides in conjunction with a peroxide co-agent.

The curing process of the present invention is carried out by bringing the terpolymers into contact, under reaction conditions, with an organic peroxide and a co-agent, and preferably a strong organic base  
 5 having a pKa greater than about 10, and preferably greater than about 12.

Organic peroxides which can be used in the present invention include a wide variety of alkyl peroxides of the type generally used in peroxide curing reactions. The organic peroxides are generally present in an amount of about from 1 to 3 parts of the peroxide per 100 parts of fluoropolymer. One peroxide curing agent which has been found to be particularly satisfactory, and is accordingly preferred, is alpha, alpha' bis-  
 10 (t-butylperoxy)diisopropylbenzene, commercially available from Hercules, Inc. This curing agent is also available from Wyrrough & Loser, Inc. in a composition comprising 40% polymeric binder, as Vul-Cup K-(VC)D-60.

A wide variety of peroxide co-agents can be used in the present invention. However, trimethylallyl isocyanurate, triallyl isocyanurate and trimethylolpropane trimethacrylate have been found to give excellent  
 15 performance, of which trimethylallyl isocyanurate is particularly preferred. The peroxide co-agents are generally present in an amount of about from 1 to 3 parts of the co-agent per 100 parts of the fluoropolymer.

It is preferred that the crosslinking reaction be carried out in the presence of a strong organic base, that is, one having a pKa of at least about 10, and preferably at least about 12. The organic base acts as an  
 20 accelerator, a processing aid and a scavenging agent, and has been found to improve the physical characteristics of the cured elastomer, including tensile properties, modulus, and compression set. One such base which has been found to be particularly satisfactory is 1,8-bis-(dimethylamino) naphthalene, commercially available from Aldrich Chemical Company as Proton Sponge. The organic bases, when used, are generally present in an amount of about from 0.1 to 1.0 parts of the base per 100 parts of  
 25 perfluoropolymer. About from 0.4 to 0.6 parts have been found to be particularly satisfactory.

The fluoropolymer compositions can also contain a wide variety of additives of the type normally used in the preparation of elastomeric compositions, such as pigments, fillers and pore-forming agents, as will be evident to those skilled in the art.

In the present curing process, the fluoroelastomer, with the required amounts of organic peroxide, co-  
 30 agent, and other components, is compounded by conventional means, such as in a two-roll mill, at elevated temperatures. It has surprisingly been discovered that the curing reaction, using the components of the present invention, can be carried out at lower temperatures than are typically used for curing using other techniques. Specifically, the process of the present invention can be effectively carried out at temperatures of about from 40 to 70 °C, and preferably about from 50 to 60 °C.

The curing times required will vary according to the particular polymer and the compound formulation  
 35 used, but a curing period of about from 15 to 30 minutes is generally found to be satisfactory. After curing, it is preferred to post cure the elastomer by heating in an inert atmosphere, such as nitrogen, for an extended period at temperatures higher than the curing temperature, according to known techniques.

The resulting cured perfluoroelastomer is characterized by a carbon-carbon crosslinking moiety, which  
 40 results in outstanding hydrolytic stability. Infrared analysis of the crosslinked compositions confirms the absence of triazine linkages which are formed using other curing systems such as TPT.

The cured compositions of the present invention exhibit a surprising stability in a wide variety of environments, including unusual resistance to degradation by water and ethylene diamine. This outstanding  
 45 hydrolytic stability is achieved without substantial depreciation of the excellent tensile properties of the elastomer. In addition, the peroxide cured elastomers of the present invention exhibit good long term thermal stability, which is particularly surprising in view of experience with other fluoroelastomers which shows a marked depreciation of thermal stability with the use of peroxide cure systems.

The instant invention is further illustrated by the following specific Examples, in which parts and percentages are by weight unless otherwise indicated.

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#### EXAMPLE 1 AND COMPARATIVE EXAMPLE A

In Example 1, a cured perfluoroelastomer was prepared by mixing, on a two-roll rubber mill at 60 °C,  
 55 100 parts of perfluoroelastomer of TFE/PMVE/8CNVE in a ratio of 56.8/41/2.2, 12 parts of carbon black SAF, 6.75 parts of K(VC)D-60 dispersion containing 2.7 parts of alpha, alpha' bis(t-butylperoxy)-diisopropylbenzene peroxide curing agent, 2 parts of trimethylallylisocyanurate peroxide co-agent, and 0.5 parts of 1,8-bis-(dimethylamino) naphthalene organic base. The mixture was milled for 20 minutes.

In Comparative Example A, the above procedure was repeated, except that the perfluoroelastomer was cured with 3 parts of tetraphenyltin at 199° C.

Samples of the resulting compounds were press-cured in an electrically heated press for 10 minutes at 177° C and post cured in a circulating nitrogen atmosphere oven under the conditions summarized in Table

5 I. The samples were subsequently tested for physical properties.

The degree of crosslinking was measured in a Monsanto Moving Disc Rheometer (MDR) at 177° C.

The MDR and physical testing results are summarized in Table I and, in Figure 1, are compared at 150, 160, and 177° C to compositions of Comparative Example A. The test results indicate that the peroxide curing agents used according to the present invention are significantly more active than TPT, as shown by 10 the higher delta torque values of the MDR measurements. Moreover, the present peroxide compounds provide excellent vulcanized perfluoroelastomer compositions which can be cured more rapidly and at lower temperatures than compositions prepared using TPT curing. The present compositions also generally attain a more complete state of cure during the conventional press curing operation and require less severe post-curing conditions of 24 hours at 232° C. The physical properties compared in Table I for the peroxide cured 15 compositions and those cured with TPT are substantially equivalent, and the present compositions are significantly more resistant to exposure to hot water.

**TABLE I**

20	<u>Example</u>	<u>Comparison A</u>	<u>Example 1</u>
	<u>Compounding</u>		
	Perfluoroelastomer	100	100
25	Carbon Black	12	12
	18-Crown-6	0.3	0.3
	TPT	3	-
30	K(VC)D-60	-	6.75
	Proton Sponge	-	0.5
	Trimethallyl - isocyanurate	-	4
35	<u>Testing of Compound</u>		
	MDR - 30 Min. Trace, <u>1°Arc</u>	<u>199° C</u>	<u>177° C</u>
40	Min.	42.1	24.0
	Max.	81.5	130.2
	Torque	39.4	106.2
	ts2	2.27	1.58
45	tc90	26.31	6.94
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TABLE I (Continued)Curing of CompoundPress Cure

Time (Min)/Temp °C	30/210	10/177
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Post Cure (under N<sub>2</sub>)(PCN 42)  
6/90

Time (Hrs)/Temp °C	10/90 to 350	24/232
	26/305	

Properties of Cured ElastomerTensile Test

M <sub>100</sub> , psi (MPa)	1017	854
T <sub>B</sub> , psi (MPa)	2192	2116
E <sub>B</sub> , %	158	184
Hardness, Shore A	83	82

Compression Set, %

70 hrs/204°C	25	39
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Volume Swell, %

Water (3 days Liquid H <sub>2</sub> O/232 ± 5°C)	24	2
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Ethylenediamine (7 Days/96-98°C)	85	19
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Claims

1. In a cured perfluoroelastomer composition prepared from polymerized units of tetrafluoroethylene, perfluoro (alkylvinylether) and a nitrile-containing monomer, the improvement wherein the perfluoroelastomer is crosslinked with a carbon-carbon linkage.
2. A cured perfluoroelastomer of claim 1 wherein the perfluoro (alkylvinylether) is perfluoro (methylvinylether).
3. A cured perfluoroelastomer of claim 2 wherein the perfluoroelastomer is polymerized from about 53-79.9 mole percent tetrafluoroethylene, 20-46.9 mole percent perfluoro (methylvinylether) and 0.1-2.5 mole percent nitrile-containing monomer.
4. A cured perfluoroelastomer of claim 3 wherein the nitrile-containing monomer consists essentially of perfluoro (8-cyano-5-methyl-3,6-dioxo-1-octene).
5. A cured perfluoroelastomer of claim 1 further characterized by an absence of triazine linkages, as determined by infrared analysis.
6. In the process for crosslinking a perfluoropolymer of the type comprising polymerized units of tetrafluoroethylene, perfluoro (alkylvinylether) and a nitrile cure site monomer by contacting the per-

fluoropolymer with crosslinking agent under reaction conditions, the improvement wherein the crosslinking agent comprises an organic peroxide and a peroxide coagent free radical source.

7. A process of claim 6 wherein the organic peroxide and the peroxide coagent are each present in an amount of about from 1 to 3 parts per 100 parts of the perfluoropolymer.

5 8. A process of claim 7 wherein the crosslinking agent further comprises about from 0.1 to 1.0 parts of an organic base having a pKa greater than about 10.

9. A process of claim 8 wherein the organic base has a pKa greater than about 12.

10. A process of claim 9 wherein the organic base consists essentially of 1,8-bis-(dimethylamino) naphthalene.

10 11. A process of claim 6 wherein the perfluoropolymer is contacted with the crosslinking agent at a temperature of about from 40 to 70 °C.

12. A process of claim 11 wherein the perfluoropolymer is contacted with the crosslinking agent at a temperature of about from 50 to 60 °C.

13. A process of claim 7 wherein the organic peroxide consists essentially of alpha, alpha' bis(t-butylperoxy)diisopropylbenzene.

14. A process of claim 7 wherein the peroxide coagent free radical source is selected from the group consisting of trimethylal isocyanurate, triallyl isocyanurate and trimethylolpropane trimethacrylate.

15. A process of claim 14 wherein the peroxide coagent free radical source consists essentially of trimethylal isocyanurate.

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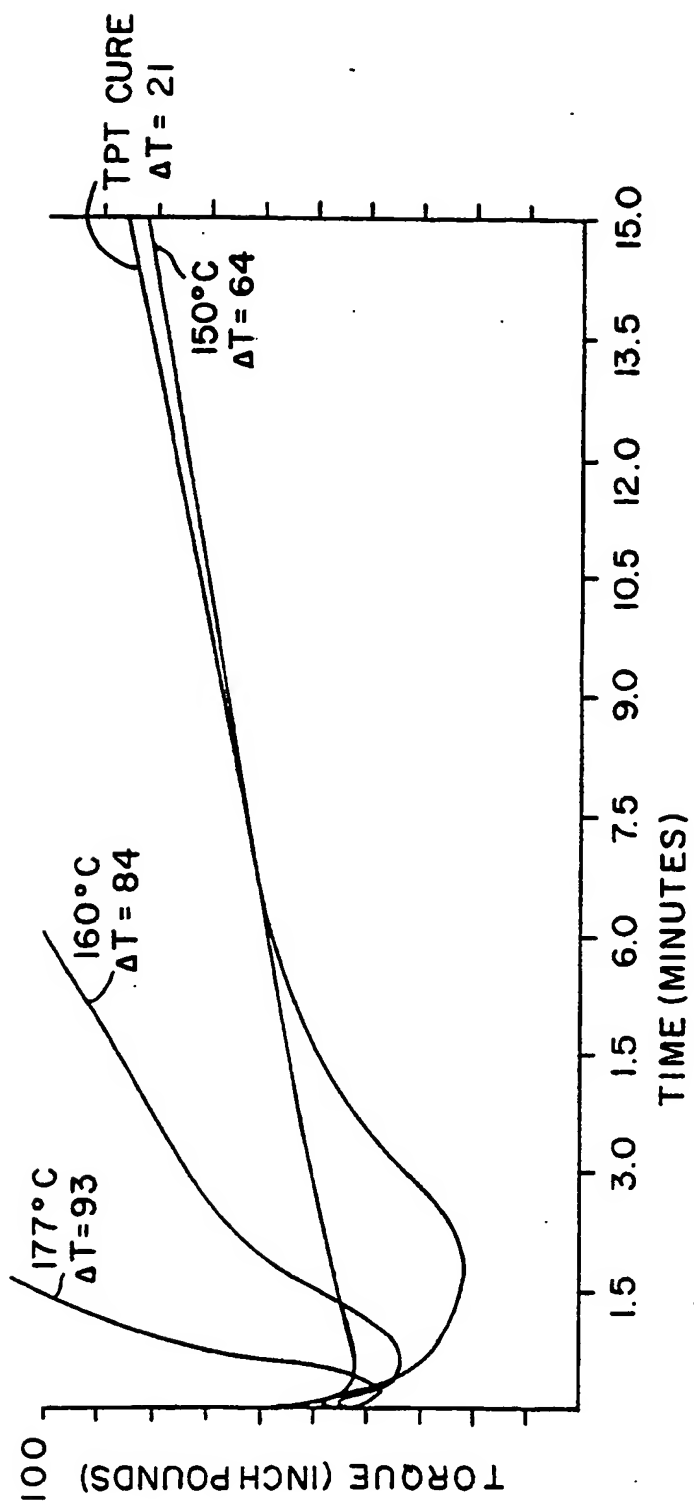
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# EUROPEAN SEARCH REPORT

Application Number

EP 89 11 9698

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 5)
A	EP-A-0 011 853 (E.I. DU PONT DE NEMOURS AND CO.) * Claims 6-10; pages 19-20; table I * -----	1	C 08 J 3/24 C 08 F 214/26 // (C 08 F 214/26 C 08 F 216:14 C 08 F 216:14 )
			TECHNICAL FIELDS SEARCHED (Int. Cl. 5)
			C 08 F C 08 J C 08 K C 08 L
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 28-06-1990	Examiner SCHUELER D.H.H.
<b>CATEGORY OF CITED DOCUMENTS</b> X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			